Replacement Halon 1301 and AFFF R&D at NRL

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Navy Technology Center for Safety & Survivability

- Span basic combustion research through shipboard fire protection systems
  - Laboratory through full size
- Combustion and suppression mechanisms and dynamics – including optical diagnostics for fluid dynamics and species concentrations
- Fire protection technology and protocol development
- Implementable systems development and validation

NAVY versus COMMERCIAL FIRE PROTECTION

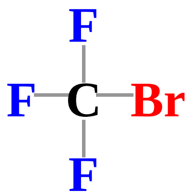
Needs are varied and different

- Missions
- Fire threats
- Fire suppression and compartment reclamation requirements
- Personnel training
- Systems reliability requirements

Fire Protection Must Maintain Mission Capability and Safety

Research Area Examples

- Halon 1301 replacement
- Aqueous Fire Fighting Foam – AFFF
- Fire Detection
- Water mist suppression
- Fire modeling
- Materials survivability



Halon 1301

1973: First large scale Navy Halon 1301 total flooding fire tests, NRL at PHILADIV

1976: NRL estimated that halon is at least as depleting to stratospheric ozone as CFCs

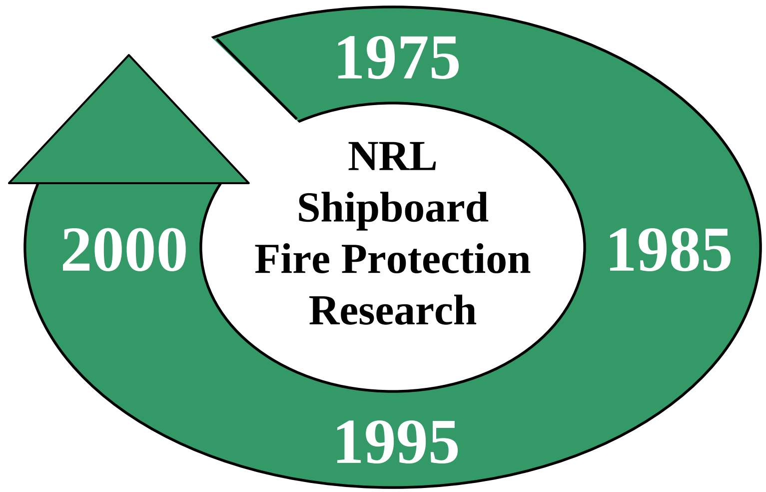
Late 1970s: Large scale Halon 1301 testing to validate use in Navy, OPEVAL TECEVAL, HF quantified

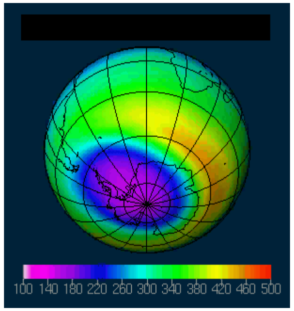
Mid 1970s: Research into suppression mechanisms, fire suppressants

Late 1970s: Halide acid gas quantificatied in small scale total flooding fire suppression

Late 1970s: Fine water mist total flooding fire suppression research

Late 1970s: Modeling physical and chemical fire suppression





1989: Montreal Protocol enters into force identifying Halon 1301 as a stratospheric ozone depleter

Late 1980s – Early 1990s: Laboratory and Large scale experiments search for a Halon 1301 replacement

Early 2000s: NRL CVN 76 fire protection system acceptance testing

Early 2000s: WSCS to be used with HFP in select compartments on LPD 17 and CVN 76, testing to provide design guidance

Late 1990s – Early 2000s: Research into acid gas reduction with water spray cooling system (WSCS)

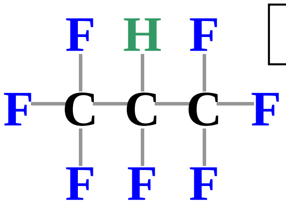
Late 1990s – Early 2000s: Testing to provide HFP design guidance

Mid 1990s: US Army: replace Halon 1301 in watercraft machinery spaces with NRL's HFP and WSCS

1996: Halon production ban

Mid 1990s: Fine water mist chosen to replace Halon 1301 in LPD 17 machinery spaces; HFP chosen to replace Halon 1301 in all other total flooding applications on LPD 17 and CVN 76

Mid 1990s: Halon 1301 replacement testing on NRL's ex-USS Shadwell. High HF production quantified. WSCS developed



HFP
(Heptafluoropropane)

CVN 76

LPD 17

ex-USS Shadwell

Halon 1301 Replacement Choosing a Clean Gaseous Agent

- Down Selection
  - Tested many materials in laboratory, 10 in field tests, and several in real scale - ex-USS SHADWELL
  - Eliminated non-condensable gases, carbon dioxide, SF_6, powders/pyrotechnics and perfluorocarbons
- Hydrofluorocarbons (HFCs)
  - 1,1,1,2,3,3,3-heptafluoropropane (HFP, HFC-227ea) recommended as best replacement clean agent for Naval ship applications
  - More hydrogen fluoride (HF) acid gas than Halon 1301 ~ 5-8X

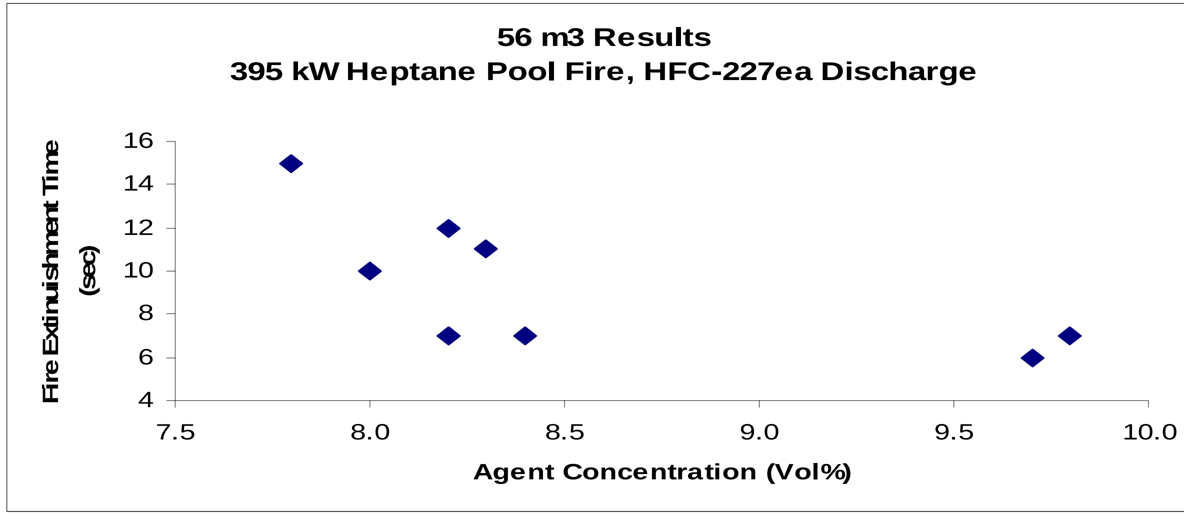
Water Spray Cooling System developed to address HF

NAVSEA 05P4 chose HFP as the optimum total flooding replacement clean gaseous agent, with WSCS for FLSRs

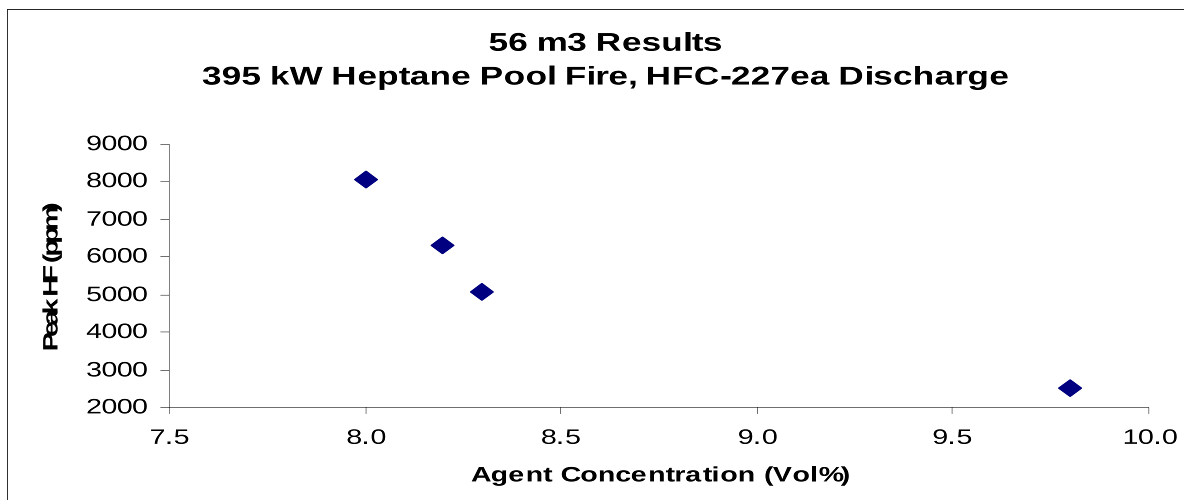
Agent Concentration Effect

56 m^3 Test Chamber

- Decreased fire extinguishment time with increased design concentration

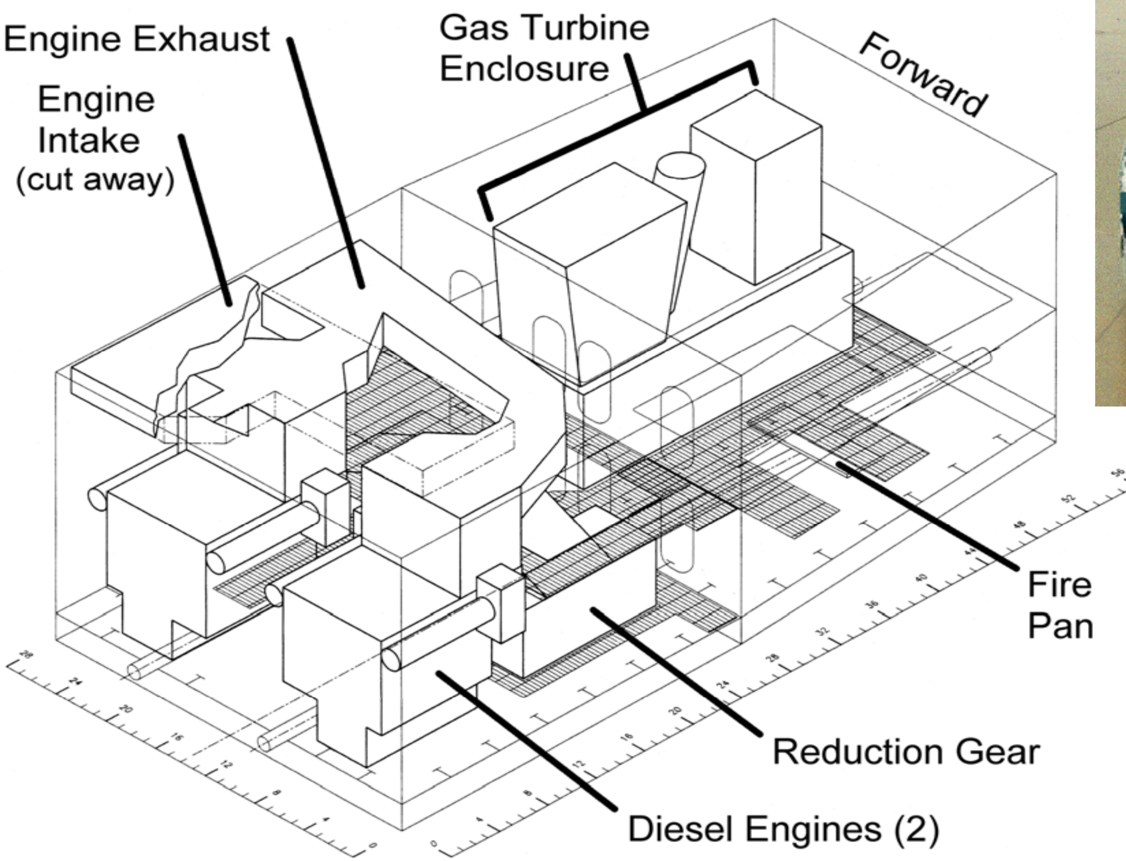


- Decreased HF production with increased design concentration



Agent concentration measured at fire at extinguishment

Full-Scale Testing in ex-SHADWELL



Total volume

594 m^3

(21,000 ft^3)

Height 6m

(20 ft)

Agents

CF_3H, C_3F_7H

Agent Distribution Questions

- 56 m^3 demonstrated design concentration effects of Halon replacements for open compartment with very little obstructions
- Real-scale tests aboard the *Ex*-USS SHADWELL showed that HFC-227ea performed very well
  - HFC-227ea chosen as the Navy's replacement
  - Engine mock-ups but mainly open spaces
  - Lasting agent inhomogeneities **> +/- 20%**

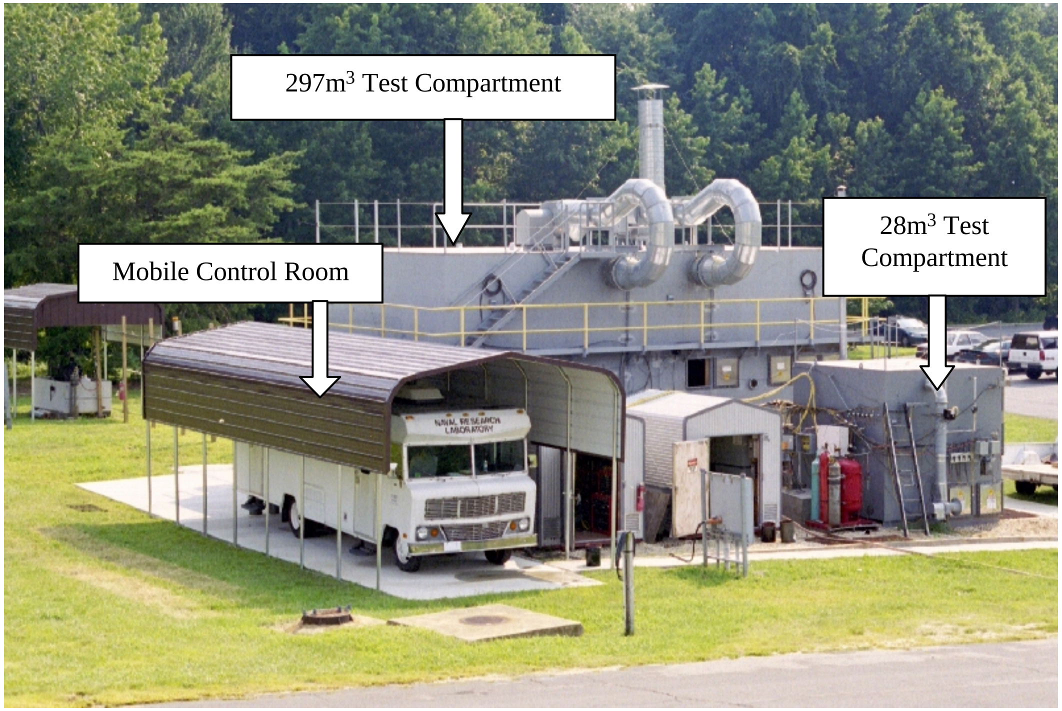
Full Scale Test Compartment Evolution

1: representative small compartment

2: maximum size for 2 nozzle system

3: representative large compartment

Volume (m3)	Length (m)	Width (m)	Height (m)
#1 28	3.05	3.05	3.05
#2 126	10.7	3.86	3.05
#3 297	10.7	6.10	4.57



Computer test control and data acquisition from Mobile Control Room

Fire Research Testbeds

28 m³ Fire Research Chamber **297 m³ Fire Research Chamber**

Flammable Liquid Store Rooms (FLSRs)

- How does HFC-227ea perform in more cluttered spaces?
- Testing conducted in a series of simulated highly obstructed Flammable Liquid Store Rooms (FLSRs)

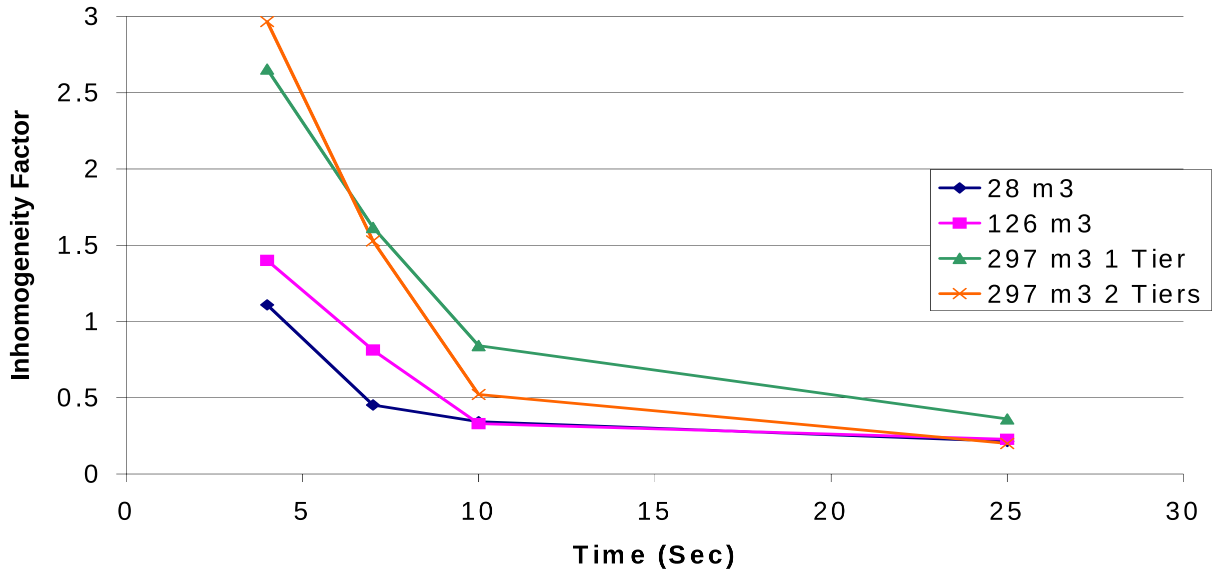
Test Compartments

Volume	Length	Width	Height	Nozzles	HF (ppm)
28 m3	3.05 m	3.05 m	3.05 m	1	**2,500**
126	10.7	3.86	3.05	2	**4,000**
297	10.7	6.10	4.57	4 (7)	**>18,000**

HF IDLH 30 ppm; NFPA re-entry guidance 90 ppm

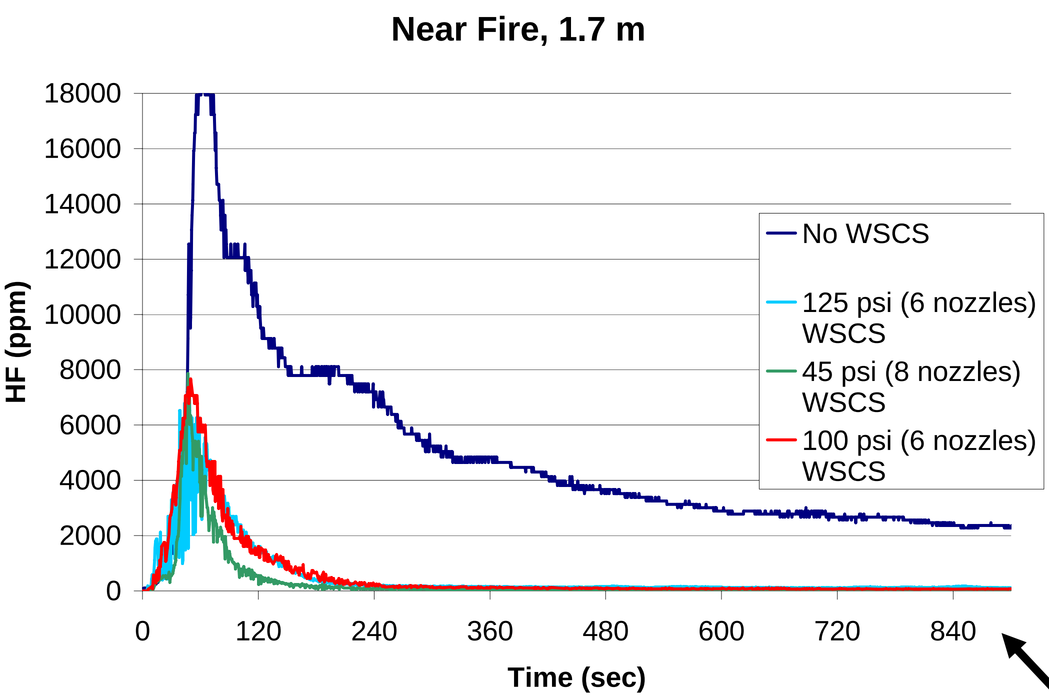
Inhomogeneities

- Determine inhomogeneities in time and space
- Measure agent concentrations during discharge at many locations

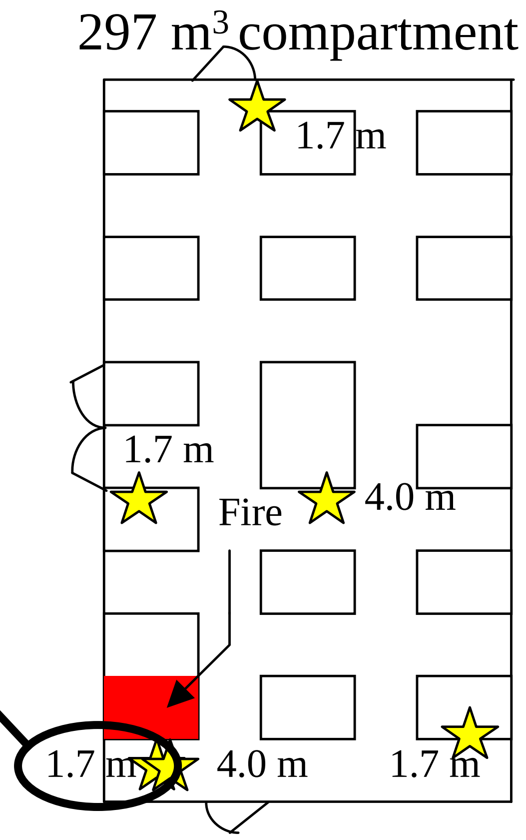


- Much more deviation in larger compartments
  - Areas of very significantly lower concentrations in 297 m^3 compartment

WSCS Effect on HF



WSCS	Peak Avg	Avg @15-min
None	12000 ppm	1400 ppm
125 psi	7500 ppm	55 ppm
100 psi	8200 ppm	60 ppm
45 psi*	7800 ppm	40 ppm



Total flow ~50Lpm

Design Guidance Summary

- HFP
  - FLSRs
    - Alcohol fire threat
    - 28 m^3: 10.5 % in overhead
    - 126 m^3: 11.5 % in overhead
    - 297 m^3: 13.0 %
      - 10.0 % in overhead
      - 3.0 % 2.9 m (> 3.8 m)
  - Machinery Spaces
    - Propulsion fuel fire threat
    - 10.2 %
- WSCS
  - Nozzles
    - K-factor 2.2 gpm/psi$^{1/2}$
    - ~<200 micron drop size
  - 8.1 m^2 WSCS nozzle spacing
    - 45 psi or greater
  - 10.8 m^2 WSCS nozzle spacing
    - 100 psi or greater

Implementation

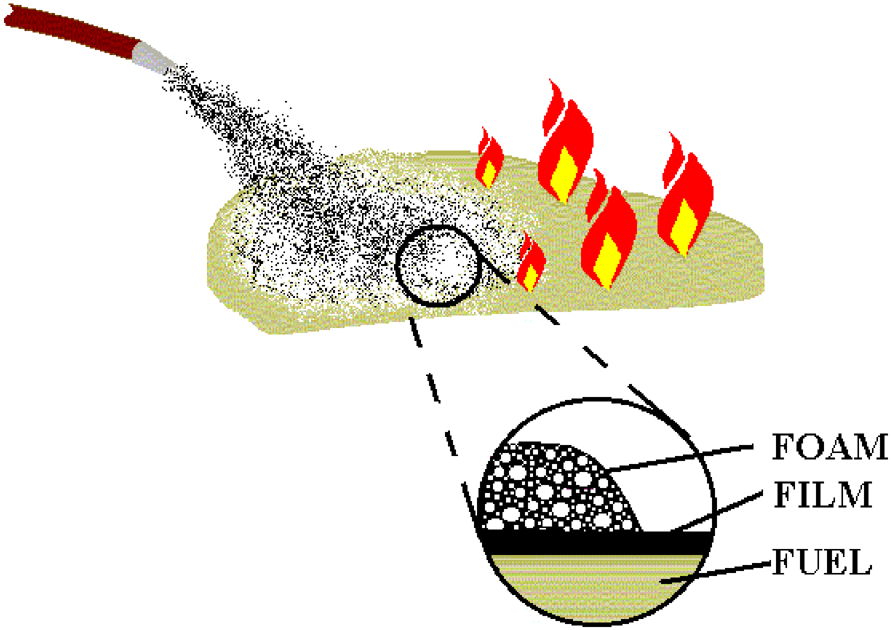
Today

- Navy employing HFP and HFP with WSCS aboard LPD-17 Class and CVN-76 Class
- Navy employing Water Mist aboard LPD-17 Class
- US Army replaced Halon 1301 systems with HFP and NRL's WSCS in over 60 watercraft machinery spaces, up to 1700 m^3 in volume

Tomorrow

- Water mist

Aqueous Film Forming Foam (AFFF)



AFFF with fluorosurfactants allows foams to form a stable liquid film on top of less dense hydrocarbon liquids, with the foam ‘floating’ on the film.

Shipboard Use of AFFF

- US Navy fire fighting foam is produced from AFFF concentrate mixed with seawater
- Vulnerability: AFFF contains organic chemicals which serve as food for microbes in seawater, allowing the aerobic microbes to consume organics and deplete dissolved oxygen
- The mixture can remain stagnant in piping for months and go into anaerobic conditions

H_2S Generation

- Once the mixture has a sufficiently low reduction–oxidation potential, Sulfate Reducing Bacteria (SRB) produce H_2S from sulfates in seawater (and AFFF)
- H_2S (rotten egg smell) is toxic (lethal) at higher doses

H_2S generation must be mitigated for safety

WITHOUT

compromising AFFF fire fighting protection

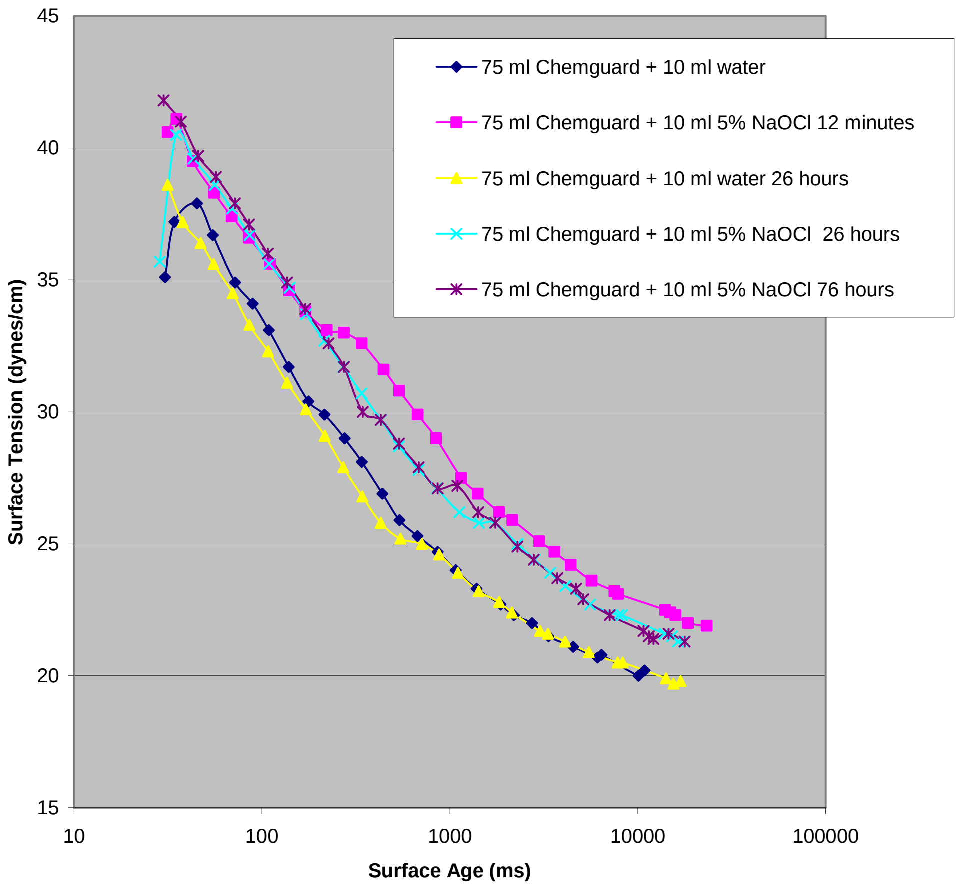
Mitigation Approaches

- Remove organic material and / or sulfates
  - ✗ Too much organics in AFFF and sulfates in seawater
- Supply oxygenation
  - ✗ Extensive engineering modifications required
- Stop oxygen depletion
  - ➡ Attack aerobic bacteria
- Stop SRB action
  - ➡ Attack sulfate reducing bacteria
- Stop sulfide from forming H_2S
  - ? Chemically react and remove sulfide

Anti-Microbials

- Oxidizing – e.g. hypochlorite
  - ✗ Consumed - no residual action, increased surface tension
- Photolytic – UV
  - ✗ Seawater opacity, need for UV transmitting windows
- Non-oxidizing
  - ✗ Sterilizer – glutaraldehyde OK but precipitate, no residual
  - ➡ Anti-bacterial agents – used in consumer hygiene products and alcohol resistant fire fighting foams (AR-AFFF)
  - ➡ Molybdate – mimics sulfate, interferes with SRB viability some effectiveness on sulfide removal

Dynamic Surface Tension



- DST characterizes surface tension as a function of surface age
- Low surface tension required for stable film on top of lower density fuel
- Hypochlorite increased surface tension

Accelerated Aging Test Mixtures

Type 6 QPL AFFF at half strength in seawater

#	AFFF Brand	Adduct	Adduct Concentration
1	National	None	-
2	National	Molybdate	5000 mg/L
3	National	Dowicil 75	2700 mg/L
4	National	Molybdate/Dowicil 75	500 mg/L/2700 mg/L
5	3M	None	-
6	3M	Molybdate/Dowicil 75	500 mg/L/2700 mg/L
7	Ansul	None	-
8	Ansul	Molybdate/Dowicil 75	500 mg/L/2700 mg/L
9	Chemguard	None	-
10	Chemguard	Molybdate/Dowicil 75	500 mg/L/2700 mg/L

Dynamic Surface Tensions (dynes/cm) at surface age of 10 seconds

Type 6 AFFF mixed at 6% (full strength) or 3% (half strength)

3M @6% Artificial Seawater	18.8
3M @3% Artificial Seawater	19.5
3M @3% Natural Seawater aged #5	19.7
3M @3% Natural Seawater+molybdate (.5 g/l) /Dowicil aged #6	19.8
Chemguard @6% Artificial Seawater	19.8
Chemguard @3% Artificial Seawater	20.7
Chemguard @3% Natural Seawater aged #9	20.5
Chemguard @3% Natural Seawater+molybdate (.5 g/l) /Dowicil aged #10	21.5
Ansul @6% Artificial Seawater	21.4
Ansul @3% Artificial Seawater	22.4
Ansul @3% Natural Seawater aged #7	22.0
Ansul @3% Natural Seawater+molybdate (.5 g/l) /Dowicil aged #8	24.2
National @6% Artificial Seawater	20.8
National @3% Artificial Seawater	22.4
National @3% Natural Seawater aged #1	28.0
National @3% Natural Seawater+Dowicil aged	28.8
National @3% Natural Seawater +molybdate (5 g/l) aged	28.6
National @3% Natural Seawater +molybdate (.5 g/l) /Dowicil aged #4	29.3

Surface tension value under ~22 required for film-forming ability on gasoline

MIL-F-24385F 28 ft^2 pool extinguishment

Initial attack, 2 gpm nozzle

MIL-F-24385F 28 ft^2 pool extinguishment

Almost extinguished, self-sealing film

Fire Extinguishment Times

Aged formulations of Type 6 QPL AFFF at half strength in natural seawater

Agent	Extinguishment (MIL Spec max 45 Sec)
3M Control	**32**
3M w/adducts	**34**
Chemguard Control	**35**
Chemguard w/adducts	**35**
Ansul Control	**43**
Ansul w/adducts	**66**
National Control	**57**
National w/adducts	**75**

Aged natural seawater test is not a MIL-F-24385F certification requirement

Results

- Fire extinguishment times correspond very well with dynamic surface tension results. DST is a proven predictor for fire extinguishment capability
- Shipboard usage compatible anti-microbial and anti-sulfate reducing bacteria agents for H_2S mitigation have been identified
- Antimicrobial and anti-SRB agents together provide H_2S mitigation in depth. The anti-microbial reduces oxygen depletion and the anti-SRB reduces H_2S generation if anaerobic conditions still occur
- At least one available QPL AFFF does not experience fire protection performance deterioration when combined with the antimicrobials

An implementable solution exists

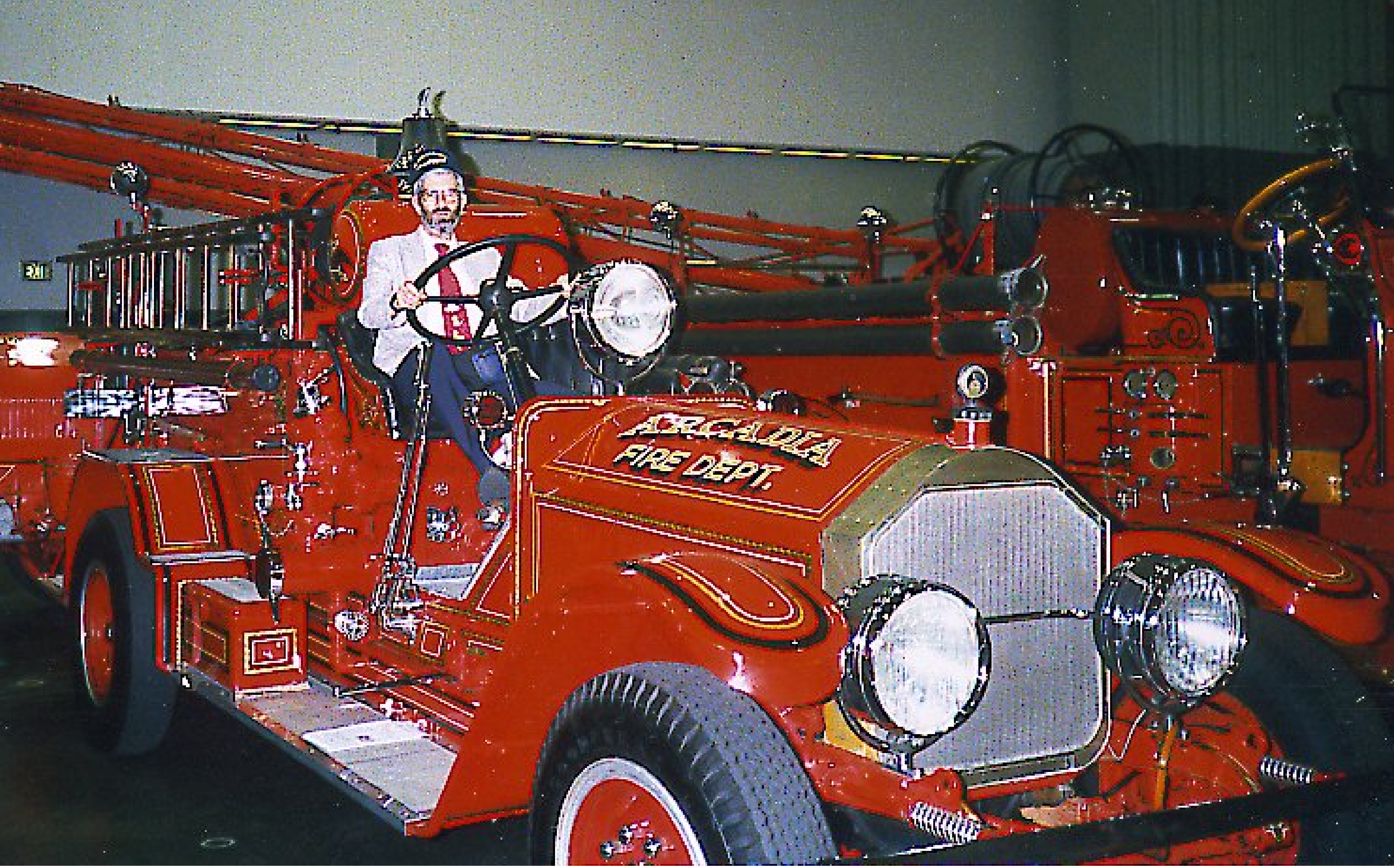
Continuing Activities

- Field and shipboard effectiveness quantification
- Development of dosing protocols and plumbing alterations
- Piping design for new construction ships to minimize potential stagnation volumes

Acknowledgements

- NAVSEA O5P4, the entity responsible for shipboard total flooding gaseous fire suppression systems and the AFFF military specification, has sponsored these efforts. Douglas Barylski is the NAVSEA lead

- These projects benefited from the contributions of many NRL personnel over the years (especially Alex Maranghides for Halon and Brad Williams for AFFF) and interactions with MPR Associates



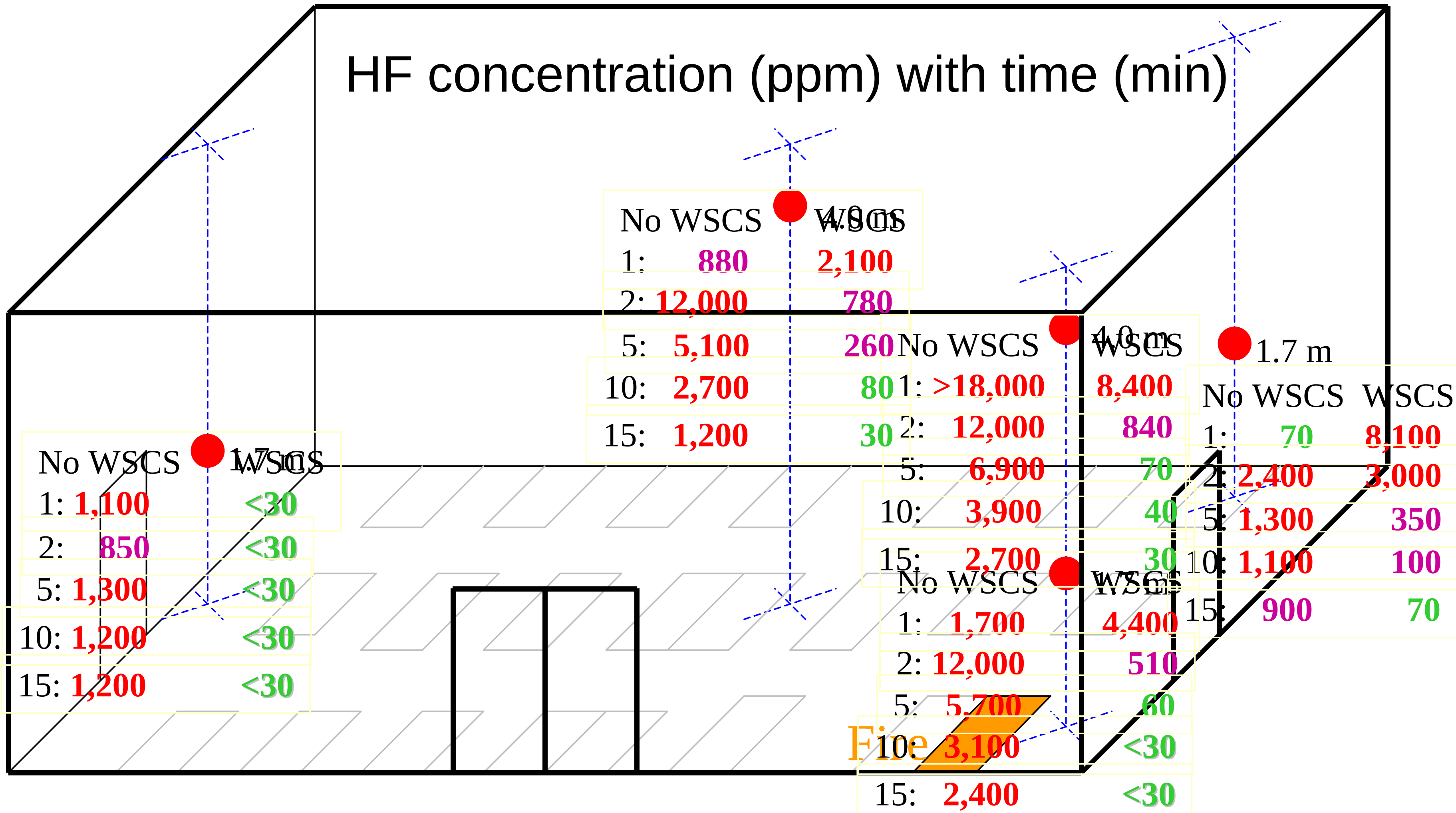
Thank you for riding along

Navy Technology Center for Safety and Survivability Combustion Dynamics Section

Summary of Methods

	Suppression Method	Advantages	Disadvantages
Halon 1301	•20 % Physical •80 % Chemical	•Very efficient •Existing design guidance	•Ozone depletion •Production ban
Heptafluoro-propane	•Mostly Physical	•'Best' chemical replacement- Navy •Guarantees extinguishment	•HF production •No cooling •Global warming potential
Water Mist	•Completely Physical	•Provides cooling •Environmentally friendly	•May not guarantee extinguishment •Distribution issues

WSCS Effectiveness On Mitigating HF



HF ppm from a 1900 kW methanol fire suppressed by HFP without and with WSCS

HFP System Design Concerns

- Agent distribution is very crucial as fires in low concentration areas will produce much more HF
- HFP is less volatile than Halon 1301
- Obstructions exacerbate agent inhomgeneities
- HFP produces much more decomposition products (HF) than Halon 1301
- Design concentration must account for inhomogeneities to minimize HF and include a safety factor

MIL-F-24385F 28 ft^2 pool burnback

Inserting burnback pan

MIL-F-24385F 28 ft^2 pool burnback

Burnback initiator pan removed

MIL-F-24385F 28 ft^2 pool burnback

Self-sustaining and growing